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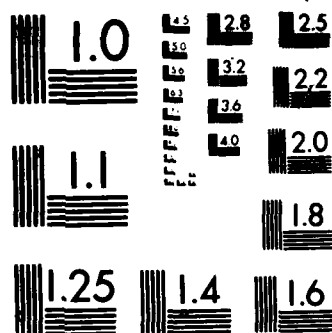
CORRELATION OF SPECTROSCOPIC AND MAGNETIC DATA OF TWO
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Spectral data for $[\text{Cu}(\text{en})_2][\text{TCNQ}]_2$ reveal a TCNQ charge transfer band at 1220 nm. With $t = 0.2$, $U = 1.3$ eV from $\Delta E(\text{CT}) = (U - \sqrt{2}t)$, then $\Delta E_{\text{ST}} = 4t/U$. The lack of a contribution of paramagnetism from TCNQ $^{\cdot-}$ to that of $[\text{Cu}(\text{en})_2][\text{TCNQ}]_2$ is understood since a system with E_{ST} of 0.12 eV would exhibit a magnetic susceptibility of 10^{-5} emu/mole at 300 K. The magnetic susceptibility of $[\text{Cu}(\text{en})_2][\text{TCNQ}]_2$ indicates that one-third an electron is transferred from from TCNQ $^{\cdot-}$ to $[\text{Cu}(\text{phen})_2]^{2+}$, and $E = 0.17$ eV. Since E and t are comparable in magnitude, the bandwidth is appreciable, and high electrical conductivities and low activation energies are expected, and observed.					
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Correlation of Spectroscopic and Magnetic Data of Two Charge
Transfer Compounds of TCNQ with Cationic Copper Chelates

by

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Correlation of Spectroscopic and Magnetic Data of Two Charge Transfer Compounds of TCNQ with Cationic Copper Chelates

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Introduction

In view of the initial work¹ on charge transfer compounds of TCNQ, one of the advantages of using copper(II) chelates as acceptors in charge transfer compounds with TCNQ would appear to be the high probability of forming stacked TCNQ⁻ segregated chains in preference to mixed CuL₂-TCNQ stacked chains. Such cationic copper chelate-TCNQ charge transfer compounds have unusual properties and have continued to attract attention.²⁻⁶

Experimental

Solid state electronic absorption spectra were obtained by using powdered samples mixed with KBr and pressed into pellets.⁷ Magnetic susceptibility data were obtained by using a Faraday balance system. The balance was calibrated with HgCo(NCS)₄⁸ and with Gd₂O₃.⁹ A value of -1.21×10^{-4} emu mol⁻¹ was used as the diamagnetic correction for TCNQ,¹⁰ Pascal's constants were used for diamagnetic corrections,⁸ and a value of 60×10^{-6} emu mol⁻¹ was used for TIP of copper(II).

Results

Electronic spectral data for [Cu(en)₂][TCNQ]₂ and [Cu(phen)₂][TCNQ]₂ along with assignments are given in Table I. Features in the electronic spectra of the [Cu(L)₂][TCNQ]₂ compounds may be understood in terms of the electronic structures of [TCNQ]_n^{q-} (q = 0, 1, 2; n = 1, 2). The spectral features probably arise from transitions at defects and chain ends, and from TCNQ⁻ + TCNQ⁻ → TCNQ⁰ + TCNQ²⁻ and TCNQ⁻ + TCNQ⁰ → TCNQ⁰ + TCNQ⁻ charge transfer.

An SCF-LCAO-MO calculation of TCNQ⁻ by Lowitz¹¹ provides the features necessary to understand the absorption spectrum of isolated TCNQ⁻. More sophisticated calculations, such as those by Jonkman and Kommandeur¹² support the spectral assignments.

Where there is overlap, the magnetic data are in good agreement with the data reported by Inoue and coworkers.⁴ The data for [Cu(en)₂][TCNQ]₂ may be fit by the Curie-Weiss law with S = 1/2, g = 2.10, and θ = 8.32. Since contributions from TCNQ⁻ molecules are not necessary to explain the

Table I. Electronic Spectral Data^a

[Cu(en) ₂][TCNQ] ₂		[Cu(phen) ₂][TCNQ] ₂		Comments
RT	77 K	RT	77 K	
365 i	355 i	370 i	370 i 415 sh	² B _{2g} → ² A _u
617 i	612 i	500 610 i 685 773	500 610 i 685 765 780	² B _{2g} → ² A _u
850 i	850 i	875 i 1000 sh	870 i 985 sh	² B _{2g} → ² B _{1u}
1220 vb	1220 vb	1170 ~2500 vb	1170 ~2500 vb	TCNQ ⁻ → TCNQ ₀ ⁻ CT TCNQ ⁻ → TCNQ ₀ CT

^aAbbreviations: RT - room temperature; i - intense; sh - shoulder; vb - very broad; CT - charge transfer; band positions given in nm.

observed data, it may be concluded that the TCNQ⁻ molecules are strongly coupled. The magnitude of the effective magnetic moment indicates that a negligible amount of electron transfer has occurred from TCNQ⁻ to the copper(II) cations.

[Cu(phen)₂][TCNQ]₂ was assumed to consist of copper(I) and copper(II) complex cations and TCNQ⁰ and TCNQ⁻ molecules within clusters or chains. The low values for the magnetic moments indicate that a substantial amount of electron transfer has occurred. If there is site preference for the electrons on the TCNQ chain, then the cluster models may be appropriate. The simplest cluster model consists of a pair, and the appropriate equation for the magnetic susceptibility is

$$\chi = 2(\rho - 0.5) \cdot (C/T) + \rho \cdot \frac{2N\mu_B g^2}{3kT} \left[1 + \frac{1}{3} \exp(-2J/kT) \right]$$

where the first term is the Curie contribution of the copper(II) complex cations, C is the Curie constant, and ρ is the degree of band filling. The quantity $2(\rho - 0.5)$ represents the fraction of copper(II) in the sample. The g value in the first term was held constant at the experimental value of 2.07. The second term is the contribution from the TCNQ clusters (pairs) with an energy gap of $2J = \Delta E_{ST}$. The g value was taken to be 2.0 for the organic radicals. The exchange coupling constant is given by the following expression:¹³

$$J = \left[\frac{t^2}{-U + (4t/\pi) \sin \pi \rho} \right] \left[1 - \frac{\sin 2\pi \rho}{2\pi \rho} \right]$$

where U and t are Coulomb and transfer integrals. This model was applied yielding $\rho = 0.71$ and $2J = -0.077$ eV. Fitting calculations were made with non-linear least squares fitting program.¹⁴

Discussion

The experimental results suggest strong intermolecular interactions between the TCNQ molecules in both copper complexes. If these molecules stack to form chains, as is common in TCNQ charge transfer compounds, then strong intermolecular interactions may not be confined to pairs of TCNQ molecules. The Hubbard model¹⁵ may be used to account for both delocalization and electron-electron repulsions (Coulomb correlations) associated with the formation of doubly occupied sites. In this model, delocalization effects are accounted for by the t_{ij} term, and localization effects through the U term.

Band Structure in $[\text{Cu}(\text{en})_2][\text{TCNQ}]_2$. The Hubbard model does not take site energy differences into consideration, and it should apply to $[\text{Cu}(\text{en})_2][\text{TCNQ}]_2$, since, by stoichiometry, all sites have one electron. Tanaka, et al.¹⁶ have shown that the energy of the charge transfer transition is given by $(U - \sqrt{2}t)$. With this relationship, the energy of the charge transfer transition (1.02 eV), and results of the calculations of $t = 0.2$ for a variety of TCNQ compounds,¹⁷ a value of 1.3 eV may be estimated for U . The effect of U is to cause a band gap at the Fermi level. Hubbard¹⁸ has determined that the gap develops for values of $4t/U < 1.15$. $[\text{Cu}(\text{en})_2][\text{TCNQ}]_2$ meets this criterion since $4t/U$ equals 0.62.

Soos and Strebel¹⁹ have determined that the singlet-triplet splitting is given by $4t^2/U$. Using the values of t and U , ΔE_{ST} is estimated to be 0.12 eV. A system with a ΔE_{ST} of 0.12 eV would exhibit a magnetic susceptibility on the order of 10^{-5} emu/mole at 300 K. A susceptibility this small could not be detected in the presence of the molar magnetic susceptibility of the $S = 1/2$ copper complex cation.

Band Structure of $[\text{Cu}(\text{phen})_2][\text{TCNQ}]_2$. When there is less than one electron per site, conductivity can occur without the formation of doubly occupied sites. Because of electron transfer from TCNQ to the copper(II) complex, TCNQ^0 sites are created, and $[\text{Cu}(\text{phen})_2][\text{TCNQ}]_2$ should exhibit properties consistent with empty-site statistics. The key to understanding the electronic structure and conductivity is provided by the low energy absorption band which arises from $\text{TCNQ}^- + \text{TCNQ}^0 \rightarrow \text{TCNQ}^0 + \text{TCNQ}^-$ charge transfer. The presence of this transition reflects a site preference, and when double occupation can be neglected, the difference in site energies dominates the conductivity process.

Soos and Klein²⁰ have modified the Hubbard model to take into account site energy differences. The modified Hubbard model yields a band structure in terms of t and E . In the case of $t \gg E$, cosine dispersion curves are obtained. In the case of $E \gg t$, the bands are flat with a gap dependent on E . The percentage of copper(II) in $[\text{Cu}(\text{phen})_2][\text{TCNQ}]_2$, as determined from the magnetic susceptibility measurements, shows that, on the average, there is about two-thirds of an electron per site. As an approximation, for this site occupancy, the energy of the charge transfer is $3E$, and therefore the site energy difference in $[\text{Cu}(\text{phen})_2][\text{TCNQ}]_2$ is 0.17 eV (0.5 eV/3). Because E and t are comparable in magnitude in $[\text{Cu}(\text{phen})_2][\text{TCNQ}]_2$, the bandwidth is still appreciable, and high electrical conductivity and a low activation energy are expected, and observed.³

Thus, the energies of the charge transfer bands $\text{TCNQ}^- + \text{TCNQ}^- \rightarrow \text{TCNQ}^0 + \text{TCNQ}^0$ and $\text{TCNQ}^- + \text{TCNQ}^0 \rightarrow \text{TCNQ}^0 + \text{TCNQ}^-$ yield data which provide an explanation of the magnetic properties of $[\text{Cu}(\text{en})_2][\text{TCNQ}]_2$ and

$[\text{Cu}(\text{phen})]_2[\text{TCNQ}]_2$ in terms of the Hubbard model and its modified variation.

Acknowledgements

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